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Project No. G-033

(U) GRAPHITE TECHNOLOGY

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Project No. G-033

(U) GRAPHITE TECHNOLOGY

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(U) GRAPHITE TECHNOLOGY

ABSTRACT

This report describes, for the period June 1 to July 31, 1958, the room-temperature properties of small specimens of molded multicrystalline graphite. The specimens are:

A pitch-bonded petroleum coke flour "standard" mix;

Several pitch-petroleum coke-thermal carbon mixes;

Mixes containing furfuryl alcohol as binder; and

A mix in which a heavy metal oxide was substituted for part of the petroleum coke.

In addition, the room-temperature properties (density, orientation factor, dynamic and static flexural moduli, ultimate flexural strength, and flexural elastic limit) were measured for a commercial, high-density (1.861 gm/cc), impregnated, molded graphite (National Carbon Company, ATJ grade).

The experimental specimens were reduced in number to approximately 500; these were graphitized to 2860°C in a nitrogen atmosphere in a single batch. Measurements of the graphitized specimens showed that:

Apparent (water) densities as high as 1.81 gm/cc can be achieved with the pitch-bonded coke flour system alone. This corresponds to a mercury density of more than 1.88 gm/cc, or about 93 per cent of the theoretical density. Still higher densities can be attained if somewhat more than 15 or less than 13 per cent of thermal carbon is substituted for petroleum coke flour; this is shown to act as a lubricant in molding and enhances shrinkage during graphitization.

The extremely low viscosity of furfuryl alcohol and the high density of the coke formed from it do not lend to the production of optimum properties with ordinary mixing, forming, and baking procedures. The experimental mixes containing this binder, however, were less vulnerable to bloating and destruction (from reduction of the heavy metal oxide) than those bonded with pitch.

In general, the density of experimental specimens exhibits the lowest standard deviation in the green state; the carbonizing process increases this two- or threefold when the binder is aged and the carbonizing cycle is slow; graphitization need not greatly increase, and may even decrease, density variation.

The room-temperature properties for ATJ graphite are reported; these will be compared with similar data for the experimental specimens in the next report.

A simple and sensitive method is described of measuring surface anisotropy by comparison of immersion densities (in water) for specimens of differing shapes.

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(U) GRAPHITE TECHNOLOGY

I. INTRODUCTION

In most of the literature pertaining to multicrystalline carbon and graphite, the scientific method chosen has been deductive; the investigator has prepared mixes in a certain way and has then compared the measured properties of specimens made from these mixes with controlled variations in composition or treatment.

While the deductive method is, in the long run, most dependable, it is unsatisfactory for this kind of inquiry for three reasons:

1) Because the carbonization and graphitization steps are slow, the deductive method becomes extremely time-consuming.

2) Because of the large number of interdependent variables which influence structure, the control of most of these while others are systematically varied, represents a difficult and expensive effort.

3) Because the properties of the green and carbonized states are profoundly and differently influenced by the graphitizing process, data cannot be fed back into the investigation until each sample series has been carried entirely through all processing steps.

It has been estimated that the development of a graphite in which a single property is absolutely optimized would require the full time of one or more men for over a hundred years - and this would have to be repeated if, for instance, the binder material were changed appreciably.

In this project, the foremost objective has been to determine whether multicrystalline graphite can, in small specimens, be regarded as an engineering material, particularly with regard to its density and strength. The assumption has been made that it would be possible to determine this simply by optimizing those factors now known to influence density and strength, keeping other factors as nearly constant as can be done in the laboratory.

This assumption cannot, of course, be rigorously confirmed, but it can be tested by simple comparison of the several properties of substantially different mixes. There are four of these.

1) The "standard" mix containing a calcined petroleum coke flour with a coal tar pitch binder,

2) A synthetic-bond mix in which the coke flour is bound with a synthetic resin,

3) A "synthetic" aggregate mix in which the aggregate is less easy to graphitize than coke flour, bonded either with pitch or the synthetic resin, whichever is better, and

4) A "carbide" mix in which a proportion of the aggregate is replaced by a heavy metal carbide.

Because so much of this work has depended upon arbitrary decisions and inductive reasoning, an extraordinary effort has been made to discuss those decisions and the reasoning which led to their adoption. In addition, an attempt has been made, where possible, to extrapolate data from the green and carbonized states and even to venture tentative predictions regarding the graphitized state.

The first series of laboratory-prepared specimens have now been graphitized and are being measured. It will be the purpose of this report to relate these measurements to previously measured properties in the green and the carbonized states, and to confirm or deny some of the principles which have been discussed. Because of funding difficulties, certain graphitized properties have not yet been obtained; it is hoped that these data can be included in later reports.

II. EXPERIMENTAL WORK AND DISCUSSION

A. Description of the Graphitizing Run

Carbonized specimens were selected on the basis of their individually measured properties (appearance, carbonized density, modulus, and volume electrical resistance) and were graphitized using the facilities of the National Carbon Company's laboratory at Fostoria, Ohio.

In the horizontal tube furnace, two graphite saggers, each approximately six inches wide and deep by 24 inches in length, were spaced equally from its center. The distance between the saggers was about 12 inches; this volume, as well as the remainder of the tube, was filled with calcined petroleum coke.

The saggers were filled with carbonized 1 x 2 x 3/8-inch specimens as follows: specimens were placed parallel to the axis of the furnace on their sides and spaced 1/8-inch apart by wires. When the layer was completed and the position of each sample recorded, the spaces between and around specimens were filled with calcined petroleum coke (about 40 mesh) from which fines had been removed. The spacing wires were then withdrawn, the

bed leveled off, and the next layer of specimens were similarly placed, spaces, and filled. With nearly a thousand specimens, the saggers each contained three layers; the upper portion of the saggers was then filled with coke, lightly tamped, and the sagger covers with a flat graphite plate of about the same thickness (3/4 inch) as that of the sagger.

In the placement of specimens, an effort was made to randomize the specimens even though thermal gradients were not expected to be large.

Temperature measurement and control were obtained at the center of the tube and the outer surfaces of the sagger ends; initial control utilized chromel-alumel couples which were withdrawn when the indicated temperature was 1060°C. Above this temperature the coke core and both sagger ends were directly observed through 3/8-inch I.D. graphite sighting tubes. Temperatures were measured using two recently calibrated optical pyrometers, interchanged among sighting positions for each observation. Maximum difference in readings was 40°C (nitrogen upstream temperature was higher) at 700°C; at higher temperatures this decreased to less than 10°C.

The heating schedule is given in Table I.

Table I

HEATING SCHEDULE - GRAPHITIZATION NO. 1

Time hr.	Time min.	Temperature (mean) °C	Rate °/hr.
-1	0	25°C (flush with dry N_2)	
0	0	start run	
1	0	700	700
2	0	1060	460
3	0	1325	265
4	0	1520	195
5	0	1740	220
6	0	1940	200
7	0	2140	200
8	0	2340	200
9	0	2540	200
10	0	2760	220
10	35	2840 (off)	80
11	0	2600	-
12	0	2275	-
		average rage	268

The charge was cooled in dry nitrogen and the saggers unpacked; each specimen was lightly brushed and returned to its envelope. It was noted that some specimens were cracked or otherwide damaged; such specimens were discarded when the damage was so extensive that grinding to one-eighth inch thickness was impossible.

B. Physical Measurements

The graphitized specimens were weighed, measured, and reweighed in water to obtain shrinkage values, bulk and apparent densities, and graphitizing loss values. These will be discussed below.

Those specimens which had previously been ground were carefully examined to ascertain whether warping had occurred.

Dynamic modulus values were obtained (using micrometer measurements to determine size and shape factors). Most specimens were then sent to the Helwig Company for grinding; they are expected to be returned as this report is being prepared.

Selected specimens were broken in flexure, and volume resistance measurements were also made for the ground specimens of ATJ graphite used for comparison purposes (see pp. 59-85, Report No. 6).

C. Comparison of Room Temperature Properties Among Mixes

A brief study of the graphitized specimens showed that the variations among water absorption effects which had been observed in the carbonized state (particularly the strongly hydrophilic nature of the furfuryl alcohol polymer) were no longer observable. All specimens absorbed about two milligrams of water after 24 hours of immersion in water containing a trace of nonionic wetting agent; further gains were negligible. Since this introduces a smaller error than that of sprayed plastic coating (from one to seven milligrams irreversible absorption) or paraffin wax (three to six mg.) it was decided to continue the use of water immersion data as the most precise values which are quickly available and which will not affect future measurements.

1. Commercial Molded Graphite (National Carbon Co. ATJ)

A block of ATJ molded graphite was cut into samples of size comparable to those being made. Earlier measurements of these samples showed an interesting variation among them in the proportion of crystallites aligned parallel to (or, in the w specimens, perpendicular to) the length and

width of the specimen.

Since the ATJ specimen was initially quite large, the molding process by which it was formed is not strictly analogous to that used to make the small 2 x 1 x 3/8-inch laboratory specimens. In a large die, a considerable variation may exist from the simple probability that any given elongated particle will tend to align itself normal to the pressing direction. The reason, of course, is that in a larger mold fairly large masses of material may flow in any direction during compaction, and this flow (or the shearing forces which attend it) tend to align the particles along the flow direction, as is observed with extruded bodies.

In general, it can be postulated that in a large molded specimen the outermost portions of the structure are most apt to be oriented normal to the pressing direction; this tendency is lessened toward the center and top of the die, where flow through longitudinal shear is most apt to obtain. Unfortunately, no record was kept of the exact location of the position of the sample ATJ block in its mold (although the direction of pressure was precisely known).

Table II gives the pertinent information for 29 ATJ specimens. It can be argued that from the tabled data specimen Nos. 1-4 and 15-19 are, from their tabled densities, unlike other w specimens cut from the same block.

In pp. 59-63 of Report No. 6, the influence of surface adsorption phenomena upon immersion density was briefly presented, and it was shown that the "water density" of a graphite specimen is influenced by its surface geometry and its anisotropy. In this report this discussion will be carried farther; in the hope that future density values in the literature will be reported in terms of the method of measurement used.

a. The Apparent Density of Graphite

The specific gravity of graphite, from careful measurements of perfect crystals, is close to 2.25 gm/cc. As stated earlier (see p. 6, Report No. 2 and reference (1) Report No. 3), the anisotropy of thermal contraction limits the true density of multicrystalline graphite to about 2.1 gm/cc.

The term "real density" is frequently used; it refers to the density of a porous body in which all external pores are filled with a fluid. In the case of graphitic structures this term is apt to be misleading, since the spaces

Table II

ROOM-TEMPERATURE PROPERTIES OF ATJ SPECIMENS
(w orientation)

Sample No.	Density (Water Immersion) gm/cc	Flexural Modulus Dynamic psi	Flexural Modulus Static psi	Vol. Resistance ohm-cm	Flexural Strength psi	Elastic Limit psi
1*	1.752	n.d	n.d	1.21×10^{-3}		
2*	1.764	n.d.	n.d.	1.22		
3*	1.761	n.d.	n.d.	1.21		
4*	1.757	n.d.	1.70×10^{6}	1.22	4790	4250
15•	1.765	n.d.	n.d.	1.19	5360	n.d.
16	n.d.	n.d.	n.d.	1.18		
17•	1.760	n.d.	1.30	n.d.	5040	3900
18•	1.764	n.d.	1.29	n.d.	5040	4200
19•	1.768	n.d.	1.32×10^{6}	n.d.	5150	n.d.
30	1.785	1.605×10^{6}	n.d.	1.21×10^{-3}		
31	1.788	1.624	n.d.	1.18		
32	1.785	1.606	n.d.	1.22		
33	1.789	1.612	n.d.	1.19		
34	1.786	1.625	n.d.	1.18		
35	1.789	1.623	n.d.	1.19		
36	1.794	1.603	n.d.	1.23		
37	1.794	1.604	n.d.	1.19		
38	1.789	1.615	n.d.	1.19		
39	1.787	1.602×10^{6}	n.d.	1.22		

* Specimens 1/4 x 1 x 2 inches
• Density specimens 1/8 x 1 x 1 inches

between ideal graphite planes may be so widely separated that some fluids may enter them. In general, when some penetration into the porous structure is involved, the term "immersion density" should be used, and the "water density", "kerosene density", "acetone density", "nitrogen density", and "helium density" of a given graphite specimen would be consecutively higher values, approaching the real density of multicrystalline graphite.

When the terms "bulk density" and "apparent density" are used, the values refer to the weight of the body in air divided by its volume. In bulk density the volume is mechanically measured or, for loose powders, refers to the fluid volume occupied. In specimen No. ATJ-3w, for instance, the dry weight is 13.897 gm. and its volume, measured with micrometer calipers, is found to be 8.189; its bulk density is thus 1.697 gm/cc.

This value includes, however, an appreciable error, since the volume thus measured includes the irregularities and intercrystalline external pores which abound on the surfaces of graphite. Despite the care used in grinding the graphite specimen, the volume is actually (when measured by displacement volumetry or weighing) greater than this. The bulk density value, then, is invariably low.

Unfortunately, it cannot be presumed to be low by a constant amount, and any measurement of displacement used must take into account any penetration or chemisorption of the displacement fluid.

Since ATJ graphite, having been re-impregnated, is too dense to be easily penetrated by mercury, mercury displacement can be used to determine the apparent volume and hence the density. Avoiding pressures high enough to force the mercury into pores smaller than 0.1 micron and tapping the specimen sufficiently to dislodge air bubbles, a series of measurements of ATJ graphite fragments were found to have a density of $1.861 \pm .002$ gm/cc.

Water is poorly absorbed, if at all, upon the planar surfaces of a graphite crystal. Since the broad areas of a w specimen predominate in crystallites thus oriented, little absorption would be expected if the w sample were very thin with relation to its width and length. The sides and ends of a graphite crystal are, however, quite hydrophilic, and one would expect a thick w specimen to adsorb more water than a thin one. As thickness is increased and length and/or width decreased the specimen shape would

approach that of the a specimens, which adsorb so much water that their immersion densities appear to be far lower (1.723 gm/cc) than those of the w specimens.

This relation can be refined to yield a more rapid and accurate estimate of "orientation factor" than has previously been available. (The "orientation factor" is a figure, usually expressed in per cent, which is for a given structure, the percentage of all crystallites which are oriented along a given axis (or plane), presuming that all other crystallites are normal to that axis (or plane). Private communications from National Carbon Company have indicated that this orientation factor for ATJ graphite is above 60 and below 75 per cent.

Table III shows a novel way of estimating the orientation factor from immersion densities of accurately machined specimens of different sizes.

Table III

WATER ADSORPTION PHENOMENON FOR ATJ GRAPHITE

Specimen Size and Orientation	Immersion Density gm/cc	Apparent Volume cc	Difference cc	Ratio	Ratio (80%)	Ratio (70%)
1/2 x 1 x 2 (w)	1.861 (Hg)	3.761	0	-	-	-
1/8 x 1 x 2 (w)	1.781 (H_2O)	3.929	0.168	1	1	1
1/8 x 1 x 1 (w)	1.764 (H_2O)	3.968	0.207	3.5	2.2	3.3
1/4 x 2 x 1 (w)	1.758 (H_2O)	3.982	0.221	3.7	2.8	3.9
1/8 x 2 x 1 (a)	1.723 (H_2O)	4.062	0.301	5.1	4.7	5.3

In this table are given the geometry and orientation of the group of specimens, their respective mean density values, the respective volumes which would be occupied by specimens of constant weight, and the differences between these volumes and the volume of mercury displaced by all specimens. In the first column labeled "ratio", the difference values are given with unity as the least adsorptive value. The last two columns show what the ratios would be if the total "active" surface of each specimen were taken to fit orientation factors of 80 or 70 per cent. By interpolation, it can be seen that these data indicate an orientation factor for ATJ graphite of about 72 per cent.

The term "active surface" simply means the area on which adsorption readily occurs. This, like the orientation factor, can readily be

estimated from moduli, thermal expansion. electrical resistance, or apparent densities. Of these the last is most easily and accurately made. Until now, however, no absolute relation has been reported for using density measurements to describe anisotropy.

The numbers in the final columns were obtained from the shape and size of the specimen:

$$\text{Active Area} = \frac{O_f - a_f + (1-O_f)(A - a_f)}{100} \qquad (1)$$

where O_f is the assumed orientation factor in per cent,

a_f is the area of the specimen parallel to the molding (or perpendicular to extrusion) pressure, and

A is the total area of the sample.

Equation (1) is an expression for the area of the specimen on which hydrophilic adsorption occurs. The ratios given in Table III relate this area to the "absorption correction" of the density equation:

$$\text{Density} = \frac{\text{dry weight}}{\text{dry weight} - (\text{wet weight} - \text{absorption correction})} \qquad (2)$$

b. The Volume Resistance of ATJ Graphite

It was found that lower, and consequently more accurate, values of volume resistivity were obtained when the thin, annealed, silver foil electrodes were polished with clean cotton muslin just prior to assembly. These are reported in Table II.

The purpose of this somewhat detailed study of ATJ graphite has been to obtain accurate and consistent data for a commercial high-density material for comparison with laboratory specimens. These data are summarized in Table IV.

2. Room Temperature Properties of Laboratory Mixes

a. Immersion Density - Standard Mix

It will be recalled that the "standard" mix is made by premixing coal tar pitch with calcined petroleum coke flour. Two such mixes were made and their green and carbonized properties were presented and discussed in earlier reports. (See in particular pp. 1-25, Report No. 6).

All of the carbonized specimens from these mixes were graphitized and their densities thereafter measured. As expected for mixes which were

Table IV

PHYSICAL PROPERTIES OF ATJ GRAPHITE

Property	Mean Value
Apparent density	1.86 gm/cc ± .002
Immersion density (in water for 1/8 x 1 x 2 specimens)	1.789 gm/cc ± .005
Dynamic flexural modulus	1.61×10^6 psi
Static flexural modulus	1.3×10^6 psi
Ultimate flexural modulus	5075 psi
Elastic limit (flexure)	about 4000 psi
Volume resistance	1.20 ohm-cm ± .03

slightly binder-deficient, some shrinkage occurred as a result of this heat treatment so that the graphitized densities are higher than those of the carbonized state.

In one case, however, a result was obtained which was quite surprising; a number of specimens were obtained whose densities in the graphitic state exceeded their green densities. It is, of course, premature to state that these are necessarily stronger than other bodies of similar density, but it is encouraging to note that a density above 1.8 gm/cc can be achieved in small specimens without impregnation.

It will be recalled that the carbonization of the standard mixes (4-1 and 3-21 series) involved several carbonizing cycles. In addition, specimens were isolated which were pressed both before and after the aging effect of heat and oxidation was linear (see graphs on pp. 3 and 7 of Report No. 6).

In Table V, the density data are organized in a similar fashion; the green and carbonized values are included (as well as the standard deviations therefrom) to provide easy comparison.

The tabled data merit some discussion. The three series, while they represent a single composition (37 parts by weight of Barrett No. 30 medium coal tar pitch to 100 parts of Texas Lockport No. 90 calcined petroleum coke) were each treated in a fashion which differed in one respect.

Mix Nos. 3-21 and 4-1 are practically duplicates except that a change (pp. 6, 8, Report No. 6) in desolvating technique for mix 3-21 apparently

Table V

APPARENT DENSITIES OF THE STANDARD MIX
(all specimens w oriented, 1/4 x 2 x 1 inch)

Specimen Series	Mold Temp. °C	Carb. Cycle	Mean Apparent Density in gm/cc					
			Green		Carbonized		Graphitized	
			Value	σ	Value	σ	Value	σ
4-1 (13-16...67)	125	a	1.760	.013	1.635	.027	1.692	.039
4-1 (14-17...65)	125	b	1.755	.017	1.617	.032	1.679	.045
4-1 (12-15...66)	125	c	1.757	.012	1.636	.033	1.684	.035
4-1 (middle group)	125	all	1.757	.014	1.629	.031	1.682	-
4-1 (pre-aged)	125	all	1.679	.039	1.545	.033	1.594	.016
4-1 (post-aged)	150	all	1.790	.004	1.707	.024	1.811	.017
3-21 (10-13...65)	125	a	1.751	.010	1.591	.026	1.660	.029
3-21 (8-11...66)	125	b	1.749	.008	1.602	.024	1.666	.012
3-21 (9-12...64)	125	d	1.752	.023	1.634	.016	1.689	.019
3-21 (middle group)	125	all	1.751	.014	1.609	.022	1.672	-
3-21 (pre-aged)	125	all	1.733	.003	1.542	.26	1.625	.015
3-21 (post-aged)	125	all	1.764	.008	1.608	.047	1.711	.032
3-21 (80 only)	150	d	1.770	-	1.682	-	1.768	-
7-16 (middle group)	125	d	1.759	.008	1.590	.038	1.643	.020
7-16 (pre-aged)	125	d	1.747	.010	1.585	.027	1.642	.044
7-16 (post-aged)	125	d	1.777	.005	1.614	.027	1.672	.020

caused a small decrease in mean green density which persists throughout later steps. Mix No. 7-16 was made in an effort to minimize, if possible, the effect of aging; the pressing period was prolonged over four days and the sigma mixer was heated but not evacuated (to minimize volatilization and oxidation). It is apparent from the table that this retention of volatiles does minimize the aging effect; the densities of the "post-aged" 7-16 series are quite comparable to the middle group of the 3-21.

With these density data in mind, it is profitable to review the relative weight losses incurred during carbonization and graphitization. (These losses are expressed as weight per cent of the specimen before heat treatment in both cases). These, together with the pertinent changes in bloat (increase in green body thickness) and shrinkage (decrease in carbonized body thickness) are given in Table VI. It should be remembered that these dimensional changes are approximate, being affected by all the difficulties of micrometry of irregular solids.

From these data it is immediately apparent that the reason for the high density of the post-aged specimens is not limited to the graphitizing process alone. While it is true that these specimens shrank more during graphitization than earlier ones, it is also true that they began as high-density bodies in the green state. It will be recalled that the post-aged specimens of mix No. 4-1 were all pressed at 150 $\pm$ 2°C, while only two specimens (Nos. 80 and 81) of mix No. 3-21 were pressed at this temperature. It is not, therefore, proper to compare the post-aged specimens of these mixes directly.

From this difference it can be inferred that maximum green density can be obtained by aging the mix to a point at which a high pressing temperature is needed; if the pressing temperature is not raised, densities will still be increased, but not as much as in the specimens pressed at a heat sufficient to drive off an appreciable percentage of volatiles.

This finding appears to be quite novel in graphite technology. It is generally assumed, for instance, that bloating (expansion) during carbonization is per se undesirable. The data for the post-aged 4-1 series show that this is the only one which bloated, all others shrank slightly. The green structure of these specimens, then, was extremely "tight" and gases could evolve only by expanding the structure. Allied with this, however, was the

Table VI

WEIGHT AND VOLUME CHANGES DURING HEAT TREATMENTS OF STANDARD MIXES

Specimen Series	Carb. Cycle	Carbonization Loss %	Carbonization Bloat %	Graphitization Loss %	Graphitization Shrinkage %
4-1 (13...67)	a	9.48	-0.42	2.63	2.78
4-1 (12...65)	b	10.96	-0.40	2.69	3.16
4-1 (12...66)	c	10.15	-0.62	2.43	2.25
4-1 (pre-aged)	all	11.12	-1.31	2.64	2.87
4-1 (post-aged) (150°C)	all	7.70	0.38	2.84	3.91
3-21 (10...65)	a	11.76	n.d.	3.10	3.13
3-21 (8...66)	b	11.27	n.d.	2.68	3.48
3-21 (9...64)	d	10.58	n.d.	2.58	3.02
3-21 (pre-aged)	all	13.09	n.d.	2.86	3.12
3-21 (post-aged) (125°C)	all	10.83	n.d.	3.25	4.09
3-21 No. 80 (150°C)	all	8.42	n.d.	2.84	n.d.

fact that: (a) a smaller proportion of gases were evolved, (b) a higher coke residue was obtained, and (c) a structure was evolved which could easily shrink during graphitization.

It will be recalled that two specimens of mix No. 3-21 were also pressed at 150°C. One of these, more than one-half inch thick, split on carbonizing; the properties of the other are sufficiently unusual (as compared with the other 3-21 series) to warrant inclusion in the tables. The apparent density of this specimen was comparable to those of similar history in the 4-1 series. Its thickness (0.580 inches) prevented measurement of dynamic modulus; the specimen has now been ground and this value will be determined.

b. Non-Standard Coke-Pitch Mixtures

Earlier mixtures were made to determine the effects of small changes in the proportion of pitch binder and in mixing or pressing procedure. Those which were expected to provide salient information were carbonized (generally on cycle d) and included in this graphitization. Of particular interest were a few specimens ground prior to graphitization to investigate the possibility of warping shrinkage during heat treatment (see discussion of stress relief,

pp. 66-82, Report No. 6).

The density (immersion) and flexural dynamic modulus values are listed for these mixes in Table VII. These confirm prior suppositions.

Some warpage was observed among these specimens, but it was confined to the hot-mixed series. It is logical to expect the residual strains in such structures to be less well distributed than in mixtures where each coke particle is initially coated with a film of binder.

Table VII

DENSITY-MODULUS VALUES, NON-STANDARD MIXES

Mix No.	Description	Immersion Density, E			
		Green gm/cc	Carb. gm/cc	Graph. gm/cc	(dynamic) psi
9-35	35 parts pitch, hot-mixed	1.612	1.494	1.583	$.89 \times 10^6$
9-38	38 parts pitch, hot-mixed	1.707	1.564	1.622	1.07
9-38 HK	38 parts pitch, solvent mixed	1.737	1.625	1.671	1.03
9-37 HK	37 parts pitch, solvent mixed	1.749	1.647	1.701	1.15

c. Coke-Thermax-Pitch Mixes

A more or less standard method of achieving high graphitization shrinkage is that of introducing a thermal black into the mixture. As stated earlier, this material is composed of nearly spherical, sub-micron particles which begin to graphitize very slowly and at high temperatures.

In an earlier report (No. 7, pp. 1-10) the green and carbonized density data are reported for six experimental mixtures which involve small variations in the proportion of thermal black (Thermax) substituted for the petroleum coke and variations in the proportion of pitch binder.

These disclosed a hitherto unreported and abrupt change in green and carbonized density with increasing Thermax in the region of 12-16 per cent substitution. It was argued that this change resulted from a change in the mode of packing of the green structure, and that a final graphitic immersion density of 1.81 gm/cc should be obtained in the 7-7 or 7-10 mix. As

shown in Table VIII, these predictions were approximately confirmed, the high shrinkage during graphitizing being sufficient to achieve 1.798 and 1.815 gm/cc, respectively.

Table VIII

DENSITY DATA - COKE-THERMAX-PITCH MIXES

Series No.	Immersion Density, gm/cc			Thermax %	Pitch parts
	Green	Carbonized	Graphitized		
7-10	1.784 (.012)	1.737 (.019)	1.798 (.010)	12	35
7-7	1.780 (.004)	1.725 (.028)	1.815 (.012)	12	37
7-12	1.777 (.008)	1.674 (.023)	1.772 (.017)	14	35
7-14	1.751 (.010)	1.641 (.021)	1.702 (.020)	14	37
4-4-1	1.783 (.005)	1.715 (.015)	1.828 (.032)	16	37
4-5	1.772 (.002)	1.705 (.014)	1.753 (.014)	16	40

(Values in parentheses are standard deviations; each series contained not less than 10 nor more than 30 specimens)

One series showed that still higher densities can be obtained. Mix 4-4-1, containing 16 per cent of Thermax, is even more "open" in carbonized structure than mix 7-7. The high shrinkage during graphitization of this mix (more than four per cent of the thickness value) should lead to excellent graphitized moduli and strength. It is expected, however, that bodies containing so much thermal carbon will, for a given density, be less resistant to thermal and mechanical shock and thermally and electrically less conductive than those in which the majority of coke particles are in intimate contact.

Table IX shows the weight losses and changes in thickness which resulted from carbonizing and graphitizing these specimens.

From the table it is apparent that the mixes of maximum density were those which shrank somewhat in both heat treatments. Further confirmation of packing theory is found in the bloat values; for a given mix the bloating (positive) is increased by increasing pitch content. Since the carbonizing loss is also increased with increasing binder content, it is not surprising that increased binder results in decreased carbonized density

throughout.

Table IX

WEIGHT AND VOLUME CHANGES DURING CARBONIZATION AND GRAPHITIZATION OF COKE-THERMAX MIXES

Series No.	Thermax %	Pitch parts	Carbonization Wt. Loss %	Carbonization Bloat %	Graphitization Wt. Loss %	Graphitization Shrinkage %
7-10	12	35	8.98	-1.37	2.41	2.89
7-7	12	37	10.34	-1.49	2.69	3.99
7-12	14	35	11.27	-1.00	2.35	3.69
7-14	14	37	11.35	.79	2.58	3.38
4-4-1	16	37	9.02	- .91	2.53	4.12
4-5	16	40	9.36	.77	2.25	2.93

As the Thermax content increases, a point is reached where the coke particles are completely interpacked with Thermax. Below this point (which appears to be about 13.5 per cent of Thermax with this grade of coke flour) the graphitizing shrinkage is determined by the resistance to shrinkage of the coke particles. Above this point, the shrinkage of the binder coke is not opposed (provided the structure is not binder-rich) because the Thermax particles are also shrinking. As a result, Thermax-rich mixtures are made more dense by a small decrease in pitch content.

Somewhere close to this critical point there are two compositions which optimize minimum carbonization loss and maximum total shrinkage. These compositions appear to lie close to the 7-7 and to the 4-4-1 mixes. If the post-aging technique is applicable to these systems, it does not appear impossible to approach the apparent graphitized density of ATJ graphite without need for impregnation. Whether such an increase in density will be reflected in increased strength (and/or modulus) is still conjectural. Theoretically, however, a stronger system will result if the maximum number of shortest, broadest bridges of binder coke can be established. This can, at present, be accomplished only by taking full advantage of the tendency of the binder to shrink as it is carbonized and converted to graphite.

d. Heavy Metal Carbide Additions

Mixtures were made containing a heavy metal oxide with (1) coke-

Thermax aggregate or (2) coke alone. Each of these was tested with the coal tar pitch binder and with the furfuryl alcohol binder. The metal was introduced as the oxide on the advice of personnel in other laboratories who have found that direct carbide additions resulted in migration during graphitization.

Unfortunately, most specimens deoxidized during carbonization, with resultant destruction of, or laminar fissions in, the specimens. Oddly enough, the majority of specimens which survived were of the coke-thermax-furfuryl alcohol type. These were, however, spongy in internal structure. Because of their heavy metal content, some of these specimens appear to have high densities, but in most cases the graphitized density was significantly lower than that of the green body. The best mix, containing 850 parts of No. 90 coke, 110 parts of Thermax, 220 parts of furfuryl alcohol monomer, displayed a green density of 1.945 gm/cc, a carbonized density of 1.907 gm/cc, and a graphitized density of 1.983 gm/cc.

These specimens are visibly poor structures. It appears that the MO_2 oxide rather than M_3O_8 should be used, despite the somewhat better thermal stability of the latter. Future work on this system is not presently contemplated, but an effort will be made to obtain some physical data with the better specimens.

In the graphitizing furnace these specimens were packed in the furthest downstream position to avoid contaminating other specimens.

e. Coke-Furfuryl Alcohol System

The use of furfuryl alcohol as a binding agent requires considerably different techniques of mixing, pressing, and carbonizing from those used with pitch or other thermoplasts (see pp. 11-15, Report No. 7). In the opinion of Foundation specialists in elastomer systems, the Durez material is not particularly suited for use as a binder, and added work should be done to determine the optimum state of polymerization for best mixing and pressing characteristics.

Thus far the best mix (No. 11-1) contains 890 parts of No. 90 coke, 110 parts of Thermax, and 220 parts of the Durez monomer to which the acid catalyst is added (three per cent of alcohol weight). The mean density values for such a mix are: green 1.708 gm/cc, carbonized 1.623 gm/cc, graphitized 1.730 gm/cc. Standard deviations from these values are not unlike those observed with the pitch-bonded specimens. Flexural moduli in the carbonized

state are higher than comparable pitch-bonded specimens (2.385×10^6 psi as opposed to 2.142×10^6 psi for the standard specimens), but this difference may not be significant.

Graphitized specimens from this and other exploratory mixes are being ground for refined measurements.

III. CONCLUSIONS AND RECOMMENDATIONS

Within the limitations of experimental work on small, molded specimens, several conclusions can now be firmly made regarding the achievement of high density.

1) For coke-flour bodies, graphitized densities in excess of 1.8 gm/cc can be attained (presumably without sacrifice of strength or resistance to thermal shock) by removing a significant proportion of the normal volatile material from a coal tar pitch binder prior to the molding operation, and molding at a temperature higher than normal. If carried to its end point, this procedure would entail:

a) Coating coke particles with a pitch film,

b) Aging the pitch film to incipient coking, and

c) Hot-pressing the resultant mixture.

It is strongly recommended that this be experimentally studied without delay.

2) For coke flour-thermal carbon bodies, graphitized densities well above 1.8 gm/cc can be attained; there are good theoretical reasons for belief that some sacrifice of resistance to thermal shock occurs when the proportion of thermal carbon exceeds about 15 weight per cent of the total aggregate. Below 13 per cent, the thermal carbon particles appear to act as a lubricant to increase green density and to enhance shrinkage during graphitization.

3) Failure to achieve high-density bodies with furfuryl alcohol is ascribable to very low viscosity and a tendency toward hydrolysis in the (largely monomeric) material studied thus far. As with all thermosetting binders, the furfuryl alcohol-bonded bodies crack or delaminate easily during carbonization. Where appreciable gas evolution must occur at moderate temperatures, however, the strength of such binders, needed to hold the body together, is considerably greater than that of thermoplastics such as pitch.

Until more data is available regarding the value of the high-density coke bonds (formed by furfuryl alcohol pyrolysis) it cannot be stated whether

such bonds will be stronger or only more brittle. It is expected that some indication of this will be obtained from flexural modulus and strength data now being obtained.

4) It is possible, by means of immersion density data alone, to obtain an estimate of the orientation of surface crystallites in specimens of varying dimensions. With ATJ graphite, this determination if more exactly made by density comparison (actually surface adsorption measurement) than by comparison of electrical resistance or modulus, since:

a) the latter data are a function of density and of structure, while the former is a function of structure alone, and

b) the measurement of resistance and modulus is difficult and, in small specimens, less exact than the measurement of density.

It is also possible, within the limitations of this study, to confirm certain assumptions regarding the effect of thermal history on graphite structure.

1) In all specimens, a freshly cut specimen is slightly higher in flexural modulus, slightly smaller in all dimensions, and slightly higher in electrical resistance (at room temperature) than it is after one or more heat treatments to above its creep threshold (usually 2150-2400°C). Such treatment is therefore recommended for engineering applications.

2) In all specimens (w) having crystallites predominantly oriented along the specimen axis, the ultimate strength is lower at room temperature than at 1500°C or higher.

3) In all specimens the flexural modulus (measured either statically or dynamically) increases with increasing temperature to above 2000°C, the rate of increase being more rapid above 1700°C than at lower temperatures.

4) With ATJ specimens (in the w orientation), the measurement of static flexural modulus is meaningless at slow loading rates above 2150°C, plastic deformation becoming appreciable at this and higher temperatures. This may be attributable to crystal growth in the compressed portion of the specimen; if this is so, the threshold of creep occurs at a lower temperature in compression than in tension. This may account for the dissimilarity in the E vs T relation for differently oriented specimens (see pp. 77, 79-81, and 83-85, Report No. 6).

IV. CONTRIBUTING PERSONNEL

The graphitizing run described in this report was made in facilities at Fostoria, Ohio, provided by the National Carbon Company. The Foundation gratefully acknowledges the skilled control and technical assistance of that company's research division.

Physical measurements and supervision of the graphitizing run were carried out by T. R. Greening. Messrs. S. A. Bortz, H. H. Lund, R. S. Olsen, and R. A. Humphrey measured physical, mechanical and electrical properties. R. S. Olsen assisted in the reduction of approximately 200,000 items of measurement and calculations on which these reports are based.

V. LOGBOOK RECORDS

Data from previous logbooks (C-6612, C-6801, C-6830, C-7000, C-7142, C-7149, C-7153, C-7264, C-7272, C-7273, C-7274, C-7665, C-7684, C-7696, C-7773, C-7804, C-7821, and C-7842 and D-1149, D-1150, D-1250, have been reduced and summarized in D-1251 and D-1252.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION
of Illinois Institute of Technology

S. W. Bradstreet, Supervisor
Inorganic Technology Section

APPROVED:

John M. Neff, Manager
Ceramics and Minerals Department